Effect of chemical modification on the properties of wood /polypropylene composites

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Abstract: Aluminate-based coupling agent was added as a compatibilizer to make the chemical modification of wood powder. The mechanical properties and morphology of wood powder/polypropylene composites were studied. The results showed that the compatibilizer can increase the impact strength of the wood/polypropylene composites, but it has a slightly negative effect on the tensile and flexural strength. For dynamic mechanical properties and Differential Scanning Calorimetry, Aluminate-based coupling agent can slightly increase the storage modulus and loss modulus, and decrease the melt point and the Calorie of Melt. Scanning electron microscopy showed that Aluminate-based coupling agent had a stronger affinity between the wood and polypropylene surfaces. These results suggested that Aluminate-based coupling agent may play a useful role in improving wood powder/polypropylene composites properties.

Keywords: Powder/polypropylene composites; Mechanical properties; Dynamic mechanical properties; Morphology
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Introduction

In recent years, many studies have been conducted on the development of reinforced polymers with wood powder due to low cost, recyclable, biodegradability, low specific gravity, abundant materials, and high specific strength and stiffness of wood (Mekenzie *et al.* 1979; Stark *et al.* 1997; Takatani *et al.* 2000; Berger *et al.* 1997; Hill *et al.* 2000). However, the compounding of wood powder with a polymer matrix often leads to poor mechanical properties of the composites. The poor mechanical properties of wood powder reinforced polypropylene composites have been attributed to: poor compatibility between the polar hydrophilic wood powder and the non-polar hydrophobic polypropylene, and weak interfacial adhesion between wood powder and polypropylene matrix (Oksman *et al.* 1995); and poor dispersion of wood powder in the polypropylene matrix due to strong powder-powder interactions resulting from hydrogen bonding. Several physical and chemical means have been used to overcome these problems (Oksman 1996; Wu *et al.* 2000; Flex *et al.* 1991; Matuana *et al.* 2001). For the chemical means, many kinds of chemical agents were used to improve the properties of the composites (Kazayawoko *et al.* 1999; Oksman *et al.* 1998; Myers *et al.* 1991). The mechanism is formation of ester bonds at wood powder surface by the coupling agent to decrease the polar hydrophilicity of the wood, and then construction of an adhesive bridge between wood powder treated and polymer matrix, thereby increasing the interfacial adhesion between wood powder and polypropylene matrix (Maldas *et al.* 1989a; Raj *et al.* 1989).

The Aluminate-based coupling agent is one of the cheaper compatibilizers compared with titanate compound coupling agent and has the same effectiveness as titanate in modification of wood powder. In this study, Aluminic ester, as a coupling agent, is used to improve the adhesion between wood powder and polypropylene. The objective of this study is to investigate the effect of the compatibilizer on improving the mechanical properties and the interphase between wood and polypropylene composites.

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Materials and methods

Materials

Polypropylene and Aluminic ester are commercially available: Polypropylene (powder) 2401, density 900 $kg \cdot m^{-3}$, MFI 2.85 $g \cdot min^{-1}$ (190°C). The wood powders were made and screened by mill machine and meshes at the laboratory, with a size of below 150 μm.

Treatment of wood powder

Before the mixture of wood powder and polypropylene, wood powder was mechanically treated with Aluminic ester (1.0% of weight of wood powder) as follows: 1 000-g wood powder was placed in a high-speed blender and heated to 110 °C with continuously stirring at 5 000 $r \cdot min^{-1}$ for 10 min, then Aluminic ester was added, and finished to the whole treatment after 5 min.

Treatment of wood/polypropylene composites

The treated wood powder and polypropylene were adequately mixed in a high speed mixer, and then compounded in a corotating twin-screw extruder, and the barrel temperature was 190°C. The extruded strands were cooled in a water bath and palletized. The compounded pellets were dried at 105°C before being injection-molded into standard test specimens at 190°C and 800 kN.

Mechanical test

All tests were conducted at normal temperature condition according to GB/T standards for plastics. Notched Izod impact test was performed according to GB/T1843. Flexural and tensile properties were determined by GB/T9341 and 1 040, and both adopted ISO standard. Five specimens were tested for each sample.

Measurement of dynamic mechanical properties

The dynamic viscoelasticity of the specimens was measured with a TA-DMA 2980 in the temperature range of -50°C to 180°C at a frequency of 1 Hz with an approximately heating rate of 2 °C · min^{-1}.

Measurement of Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) was performed with a Shimadzu DSC60 at a heating rate of 10 °C · min^{-1}.

Scanning electron microscopy

The samples were divided into two parts. One was kept in original state, and the other was treated with concentrated sulfuric acid and a mixture of hydrogen peroxide/acetic acid at room temperature to remove cell wall materials completely (Fujii *et al.* 2000). All specimens were coated with Pt in an ion-sputter coater at 1.5 keV for 7 min. The specimens were observed at three directions on the same sections by the scanning electron microscopy.

Results and discussion

Mechanical properties

The mechanical properties were measured to show the reinforce ability of wood powder as a filler in the composites. The comparison of mechanical properties of the composites with different ratio of wood powder and the PP (Polypropylene) is shown in Table 1. The results show that the tensile strength and flexural modulus of elasticity of the composites are improved compared with those of the pure PP, but Izod impact is reduced if the wood powder is not treated with the compatibilizer. The wood powder treated by Aluminic ester has a slightly negative effect on the tensile and flexural strength of the composites, but it can improve the impact strength and flexural modulus of elasticity of the composites (see Table 1).

Table 1. The comparison of mechanical properties of pure PP (polypropylene) and wood powder-PP composites with different wood powder contents and wood powder treated by Aluminic ester

Items	Tensile strength (MPa)	Flexural strength (MPa)	Flexural modulus of elasticity (GPa)	Izod impact (notched) J/m
Pure PP	29.1	47.5	1.33	20.0
50% wood powder+50% PP	36.4	51.1	3.60	14.4
50% wood powder (treated by Aluminic ester) +50% PP	31.1	42.3	3.68	26.8
60% wood powder (treated by Aluminic ester) +40% PP	29.4	37.1	3.72	25.4

Dynamic mechanical properties and Differential Scanning Calorimetry

The interaction between wood powder and polymer in the composites can be obtained by the measurements for dynamic mechanical properties of composites, and their interaction at the molecular level can be provided based on the position of the primary peaks in the damping curve (tanδ). Moreover, the peak position of the damping curve can also provide an insight to the impact behavior of materials. In order to obtain information about molecular motions of the composites and the effect of chemical modification of wood powder treated by the compatibilizer, the dynamic mechanical properties of the composites specimens with 50% wood powder by weight were measured at 1 Hz, which the wood powder was separately treated and untreated with the compatibilizer. The damping (tanδ), storage modulus (G'), and loss modulus (G") of the composites with and without the treatment by the compatibilizer as functions of temperature are shown in Fig.1. The addition of the compatibilizer results in slight increases o f storage modulus and loss modulus (Fig.1). The temperature dependencies of the dynamic mechanical properties of pure polypropylene and composites filled 50% and 60% wood powders, which also were treated with compatibilizer, is shown in Fig. 2. The curves show that the more the wood content in the composite is, the higher G' and G" of the composites are, and the lower glass transition temperature of the composites is.

The additions of wood powders and the compatibilizer can both improve the viscoelasticity of composites (Figs. 1 and 2). Compared with wood powder, addition of the compatibilizer made glass transition temperature (T_g) shift to a higher temperature. This indicated addition of the compatibilizer made more difficulty of micro-Brownian motion of polymer chain segments. As a result, the composite needed a higher temperature to initiate its micro-Brownian motion.

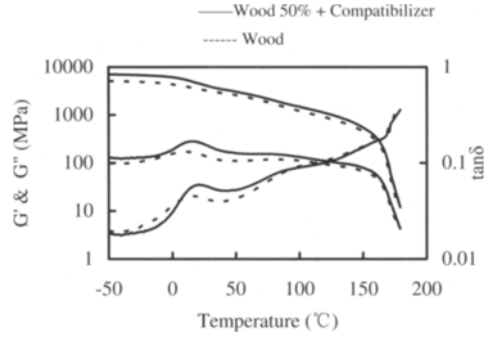

Fig.1 G', G" and tan δ vs. Temperature curves for 50% wood powder-filled composites treated and untreated with the compatibilizer

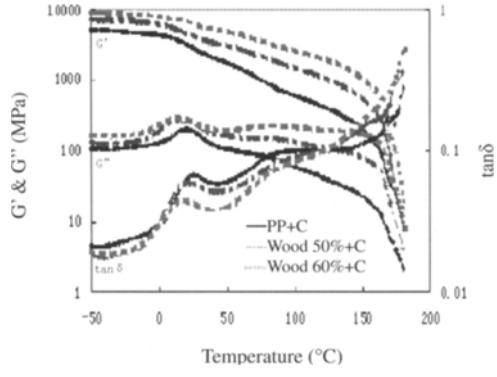

Fig.2. G', G" and tanδ vs. Temperature curves for PP, 50% and 60% wood powder-filled composites treated with the compatibilizer

The melt points and Calorie of Melt of different composites were measured by the Differential Scanning Calorimetry. The results are illustrated in Table 2. For pure PP, the melt point decreased, and the Calorie of Melt increased at the addition of the compatibilizer. For the composite filled 50% wood powder, Calorie of Melt clearly decreases (from 83.7 $mCal \cdot mg^{-1}$ to 73.2 $mCal \cdot mg^{-1}$), but the melt point remains almost constant.

Table 2. Comparison of melt points and Calorie of Melt of different composites

Items	PP	PP+C	50% wood	50% wood+C
Melt point (℃)	167.24	165.81	164.84	164.80
Calorie of melt (mCal/mg)	74.9	83.7	83.7	73.2

Morphology of polypropylene/wood powder composites with and without the compatibilizer

The effect of compatibilizer on the morphology of the composite can be obtained by detecting the surfaces of the composites with scanning electron microscopy. The interfacial region between the PP matrix and wood filler was investigated. The microstructures of the composite without compatibilizer show that a wood particle embeds in the polymer matrix (Fig. 3). The wood powder particles are well dispersed on the PP matrix. But big gap can be seen between the wood surface and the PP matrix. The voids around the particle indicate poor interaction between the wood surface and the PP matrix.

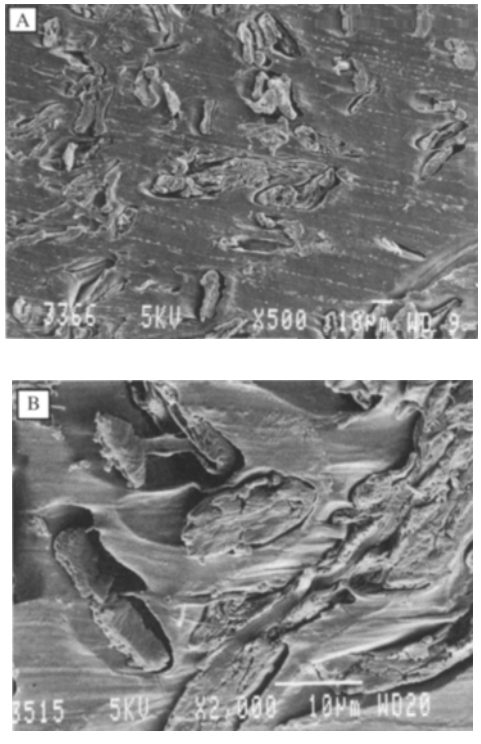

Fig. 3 SEM micrograph of composite with 30% wood but without compatibilizer.

A: Wood powder particles were well dispersed on the PP matrix;

B: Interface/interphase region between the wood powder and the PP matrix.

The microstructures of the composite with compatibilizer are different from those of the composite without compatibilizer (Fig. 4). Generally, it is rather difficult to differentiate wood particles from the PP matrix. This may suggest that the wood particles are coated by the compatibilizer, and the adhesion between the PP and the wood is good. It is considered that the mechanical properties could improve because the impact strength of the composite has been improved. In fact, the impact strengths of the composite without and with compatibilizer are separately 22.4 $J \cdot m^{-1}$ and 26.8 $J \cdot m^{-1}$ at wood content accounting for 50% of the composites. This also suggests that certain interfacial contact between the wood powder and the PP and loads can be transferred from the matrix to the wood filler.

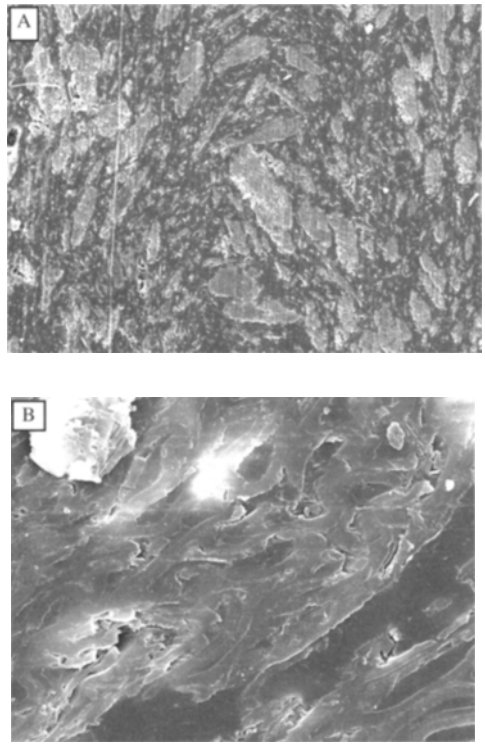

Fig. 4 SEM micrograph of composite with 50% wood but with compatibilizer.

A: Wood powder particles were well dispersed on the PP matrix;

B: Interface/interphase region between the wood powder and the PP matrix.

The microstructure of the composite with compatibilizer and with wood content of 50% and 60% is shown in Fig.5. There is no difference in the interface region between the wood powder and the PP matrix. The microstructure of the composite after removing the wood is shown in Fig.6. On the basis of those photos, it is clear that ray parenchyma cell appeared to be well impregnated with PP and the shapes of pit cavities were clearly projected from PP molding cell.

Conclusion

Aluminic ester as a cheaper compatibilizer can improve the impact strength of the wood/polypropylene composites, but it has a slightly negative effect on the tensile and flexural strength of the composites. It also can result in slight increases of storage modulus and loss modulus of the wood/polypropylene composites, and the decrease of the Calorie of Melt of the composites,

but the melt point remains almost constant. The addition of Aluminic ester can also improve interfacial contact between the wood powder and the polypropylene composites, and the increase of the impact strength of the composites.

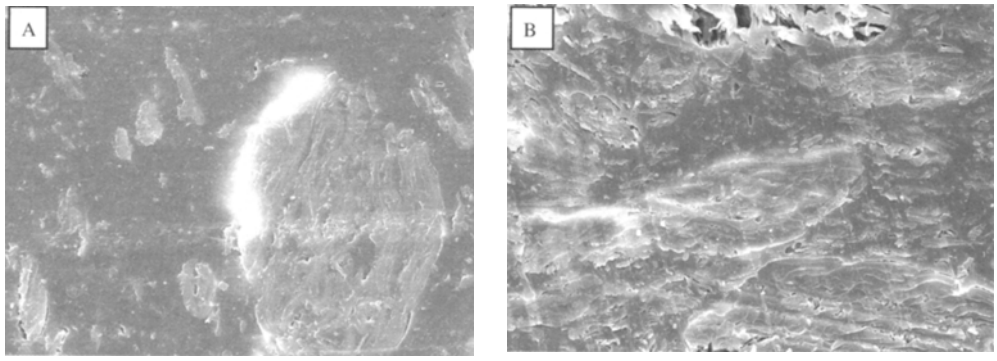

Fig. 5 SEM micrograph of composite with compatibilizer. Interface/interphase region between the wood powder and the PP matrix
A: with 50% wood content; B: with 60% wood content.

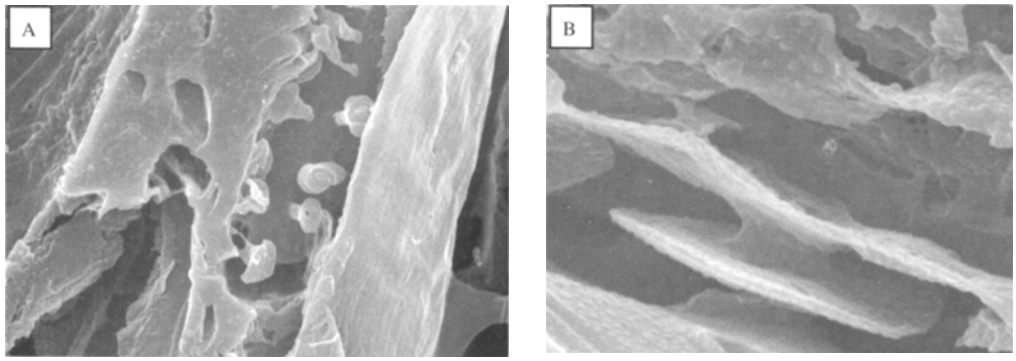

Fig.6 SEM micrograph of composite after removing the wood.
A: with 50% wood content; B: with 60% wood content.

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